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Determination of the Electronic Density of States of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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# Determination of the Electronic Density of States of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We report precise measurements of the enthalpy of polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at high temperatures ( $300 \text{ K} < T < 700 \text{ K}$ ). From these data, we determine the lattice and electronic contributions to the specific heat. We find that anharmonicity must be included when calculating the lattice specific heat. We also find that the specific heat of the charge carriers follows the temperature dependence of a Fermi liquid with a Sommerfeld constant of  $40 \pm 5 \text{ mJ/mol} \cdot \text{K}^2$ . This value is three times larger than expected from band structure calculations.

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Much effort has been focused on experimentally determining the value of  $\gamma_B$ , the coefficient of the electronic specific heat, for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .<sup>1,2</sup> An experimental measure of  $\gamma_B$  is needed to test the theoretical models for the band structure in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Also, the value of this parameter is needed to determine the relative size of the specific heat jump at  $T_c$  so that theoretical models of the superconducting state can be tested. Despite the importance of and the level of this effort, the value of  $\gamma_B$  must be judged to be uncertain as estimates range from 13 to 35  $\text{mJ/mol}\cdot\text{K}^2$ .<sup>1,2</sup>

Several groups have attempted to determine  $\gamma_B$  from specific heat data measured between the superconducting transition temperature ( $T_c$ ) and 300 K.<sup>1,2,3</sup> However, the electrons contribute only 1% to the specific heat in this temperature range, with the remainder due to the lattice. Therefore, the lattice contribution would have to be calculated with an accuracy difficult to attain in order to determine the electronic specific heat from normal state measurements below 300 K.

At high temperatures ( $T > 300$  K), the lattice specific heat approaches the classical limit, while the electronic contribution continues to increase linearly. Thus, the possibility for accurately modeling the lattice contribution improves, and the electronic term grows into a larger fraction of the total. Two groups<sup>4</sup> have measured the specific heat of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at high temperatures using differential scanning calorimetry. This method lacks the necessary accuracy to determine the electronic

specific heat. We have therefore used a phase-change calorimeter to measure the temperature dependence of the enthalpy of polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  between 300 K and 700 K. The data are sufficiently accurate that the electronic contribution can be determined by subtracting the lattice specific heat ( $c_v^l$ ) calculated from the phonon density of states. We shall show that the role of anharmonicity is significant in the lattice specific heat, and the electronic contribution is larger than previously estimated.<sup>2</sup>

The structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  forms two subsystems:  $\text{CuO}_2$  planes which extend in the a and b directions and  $\text{CuO}$  chains which follow the b-axis.<sup>5</sup> The oxygen on the chain-sites <sup>along the b-axis</sup> is much more volatile than on the plane-sites, so the oxygen deficiency,  $\delta$ , is mostly due to vacancies in the chains. The electronic properties are observed to be extremely sensitive to the oxygen stoichiometry. Hence, we have been careful to prepare samples with a small value of  $\delta$  and to measure the specific heat under such conditions that oxygen is not lost during the course of the experiment.

Polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was prepared by solid-state reaction in air of stoichiometric quantities of  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}_2$ , and  $\text{CuO}$  to yield approximately 40 g of product. Reactants were mixed before each heating by grinding for 50 minutes in an agate mortar and pestle. Two heating cycles were carried out in an alumina combustion boat: 1) Heat to 880°C in 3h, anneal 24h, furnace cool; 2) Heat to 950°C in 3h, anneal 15h, cool in 8h to 650°C,

cool in 8h to 450°C, anneal 12h, cool in 8h to ambient. The fully reacted powder was then annealed at 450°C for 24h in flowing oxygen. The product was a pure phase according to X-ray powder diffraction, all observed reflections matching those of the reported powder pattern.<sup>6</sup> Least squares refinement of the powder data yielded the following lattice parameters:  $a = 3.8838(8)$ ,  $b = 3.8164(4)$ , and  $c = 11.664(1)\text{\AA}$ . Bromo/iodimetric titration<sup>7</sup> of the powder indicated an oxygen content of 6.98 per mole compound (i.e.,  $\delta = 0.02$ ). DC magnetic susceptibility measurements showed the onset of superconductivity at 92 K with a 10 to 90% transition width of 6 K. We observed that 45% of the flux was expelled when the sample was cooled from 100 K to 4.2 K in a 0.002 tesla field.

The method for measuring specific heat by means of phase-change calorimetry is described fully in Refs. 8. The sample (mass: 4.7g) is encapsulated with exchange gas in a Pt-10%Rh vial. (We chose 33 kPa of  $O_2$  at 300 K so that the oxygen content of the sample would not change when the sample was heated.) The encapsulated sample is heated to thermal equilibrium in a furnace, and then dropped into a calorimeter immersed in a high purity ice bath. The enthalpy released by cooling the sample from  $T$  to 273.15 K melts a proportional volume of ice. The relative enthalpy is then calculated from the change in volume of the water-ice system employing an independent electrical calibration. The measured values of the relative enthalpy of

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $H_p(t) - H_p(0)$ ) are plotted vs. temperature ( $^{\circ}\text{C}$ ) in Fig. 1.

We note that this method accurately measures the enthalpy between a temperature  $T$  and 273.15 K. The sample temperature is known to within 10 mK and enthalpy changes are measured with an imprecision of 0.5 J. The enthalpy of the empty cell is measured in a second experiment. For the measurements reported here, the addenda contribute half of the total enthalpy over the entire temperature range. The estimated overall inaccuracy of an individual enthalpy datum is 0.5%. Specific heat data derived from the enthalpy are estimated to have an inaccuracy not exceeding 1%.

We calculate the average specific heat ( $\bar{c}_p = \Delta H_p/t$ ) for each datum of Fig. 1 and fit these values with the function  $a + bt + ct^2$ , where  $t$  is the Celsius temperature. The true specific heat values are calculated from the relation,

$$c_p = \bar{c}_p + t(d\bar{c}_p/dt) = d\Delta H_p/dt = \Delta H_p/t + bt + 2ct^2 \quad (1)$$

Finally, we calculate the specific heat at constant volume ( $c_v$ ) by subtracting the dilatation correction,  $\beta^2 BVT$  ( $\beta$  is the volume thermal expansion coefficient ( $36 \times 10^{-6} \text{ K}^{-1}$ )<sup>9</sup>,  $B$  is the bulk modulus ( $10^{11} \text{ Pa}$ )<sup>10</sup>,  $V$  is the molar volume ( $1.04 \times 10^{-4} \text{ m}^3/\text{mol}$ )<sup>5</sup>, and  $T$  is the absolute temperature. (The temperature dependence of  $\beta$  and  $V$  has been shown to be small between 300 K and 700 K,<sup>11</sup> but the temperature dependence of the bulk modulus, which we

assume to be constant, has not been measured above 300 K.) The resulting values for the specific heat at constant volume are plotted in Fig. 2. Note that the specific heat data measured below 300 K<sup>12</sup> (smaller circles) are in good agreement with the higher temperature data.

The coefficients of Eq. 1 have been tested for uniqueness by fitting  $H$  vs.  $t$  to a polynomial,  $at + bt^2 + ct^3$ . We find slightly different values for  $a$ ,  $b$ , and  $c$ , because more weight is given to the higher temperature points in the fits of  $H$  vs.  $t$  than in the fits of  $H/t$  vs.  $t$ . Nevertheless, the difference between the  $c_v$  vs.  $T$  curves calculated from the two sets of fit parameters is slight.

We calculate the lattice contribution to  $c_v$  from the phonon density of states,  $F(\omega)$ , determined from the measured neutron density of states,  $G_{\text{neut}}(\omega)$ .<sup>13,14</sup> We calculate the harmonic contribution to the heat capacity by directly integrating the contribution of each mode in the phonon spectrum according to the formula,

$$c_v^I = \hbar^2 \frac{d}{dT} \left( \int_0^\infty d\omega F(\omega) \omega f_b(\omega, T) \right), \quad (2)$$

where  $f_b(\omega, T)$  is the Bose-Einstein distribution. When this lattice component is subtracted, we are left with the electronic contribution to the specific heat seen in the inset of Fig. 3.

If the charge carriers pair to form bipolarons in the normal state,<sup>15</sup> we would expect the electronic specific heat to be

similar to that of a Boson gas. That is, the specific heat should peak at the condensation temperature ( $T_c = 92$  K in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ) and then decrease monotonically to the equipartition value.<sup>16</sup> Our data are therefore inconsistent with this model. As shown in the inset of Fig. 3, the temperature dependence of the electronic contribution is characteristic of the specific heat of a normal Fermi liquid, except that a line fitted to the data does not pass through the origin. The negative intercept implies that the contribution of Eq. 2 overestimates the lattice specific heat, probably due to the effect of lattice anharmonicity. Theoretical calculations,<sup>17</sup> Mossbauer effect measurements,<sup>18</sup> and the anomalous pressure dependence of the compressibility<sup>19</sup> all show evidence of anharmonicity in the zone-center phonons. This suggests that the harmonic approximation is inadequate.

The energy of an atom in a periodic potential well can be written  $E = p^2/2m + \alpha q^n$  ( $n$  is an even integer greater than or equal to zero,  $n = 2$  for a harmonic potential). Hui and Allen<sup>20</sup> have shown that a quartic anharmonicity reduces the high-temperature specific heat relative to the value expected from a harmonic potential. In fact, the equipartition value for the specific heat per mode is  $k_B(1/2 + 1/n)$ ,<sup>21</sup> for an atom in a potential,  $\alpha q^n$ . Clearly, the specific heat for purely harmonic modes will reach the Dulong-Petit limit ( $k_B$  per mode). However, the Dulong-Petit value overestimates the contribution to the specific heat from terms in the interatomic potential with  $n > 2$ .

Since the exact nature of the anharmonicity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  is unknown at this time, we propose a simple model that accounts for the anharmonicity in a way that produces a physically reasonable electronic specific heat: the interatomic potential for a fraction,  $n_a$ , of the phonons with energies less than 20 meV is quartic. Thirty percent of the phonons lie below 20 meV and these will have reached the equipartition limit ( $0.3 \times 3R \times (1/2 + 1/n)$ ,  $R$  is the universal gas constant) by the temperature, 300 K. The total specific heat for temperatures greater than 300 K can then be written:

$$C_V^1 = 0.9R(1 - n_a) + 0.675Rn_a + \hbar^2 \frac{d}{dT} \left( \int_{0.02/\hbar}^{\infty} d\omega F(\omega) \omega f_b(\omega, T) \right). \quad (3)$$

Clearly, as  $n_a$  is increased, the lattice specific heat will be reduced.

By varying  $n_a$  until the electronic specific heat extrapolates to the origin, we determine the electronic specific heat plotted in Fig. 3. If the upper and lower lines bracket the electronic specific heat, we find that  $n_a$  is  $0.25 \pm 0.08$  and the slope,  $\gamma_B$ , is  $40 \pm 5 \text{ mJ/mol} \cdot \text{K}^2$ . This is higher than other reported values<sup>2</sup>, the highest of which are in the range, 20 to 35  $\text{mJ/mol} \cdot \text{K}^2$ . These estimates for  $\gamma_B$  are determined from specific heat data measured below 300 K: a temperature range in which the lattice specific heat is difficult to model.

The measured Sommerfeld constant,  $40 \text{ mJ/mol} \cdot \text{K}^2$ , differs from the value of  $13 \text{ mJ/mol} \cdot \text{K}^2$  obtained from band structure

calculations.<sup>22</sup> This discrepancy could be due to the complicated band structure in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The Fermi energy lies near the foot of a peak in the calculated electronic density of states,  $D(\epsilon_F)$ .<sup>17</sup> Hence, sample stoichiometry, defects, or inaccuracies in the calculation could shift the electronic structure enough to raise  $D(\epsilon_F)$  to a value more consistent with our measurements.

The implications of a large value for  $\gamma_B$  are best understood in terms of a two band model. The resistivity of untwinned single crystals<sup>23</sup> shows the existence of two conducting bands: one attributed to the chains and the other to the planes. These same data show that the major fraction of the current is carried by the chains. Other studies<sup>24</sup> have shown that as  $\delta$  increases from 0 to 0.2,  $T_c$  remains nearly constant and the valence bond sum of the plane copper atoms changes very little. Thus, when a small amount of oxygen ( $\delta \leq 0.2$ ) is removed, the electronic properties of the chains are more strongly affected than those of the planes. Evidence that the chain band contributes greatly to  $D(\epsilon_F)$  is seen in specific heat measurements of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with  $\delta = 0.02$  and  $\delta = 0.2$ .<sup>25</sup> The difference between the specific heat of these two materials is linear in temperature with a slope, 32  $\text{mJ/mol}\cdot\text{K}^2$ . By identifying slope of this difference with the electronic specific heat of the chain band, we utilize our maximum value of  $\gamma_B$  (i.e.  $\gamma_{\text{ch}} + \gamma_{\text{pl}}$ ) to estimate that  $\gamma_{\text{pl}} \leq 13 \text{ mJ/mol}\cdot\text{K}^2$ . Thus the plane-carrier effective mass (in two dimensions,  $m_{\text{pl}}^* = (3/\pi)(\hbar/k_B)^2 d \gamma_{\text{pl}}$ , where  $d$  is the interplanar distance)<sup>26</sup> is less than  $9m_e$  ( $m_e$  is the free-electron mass).

The ratio of the Sommerfeld constants for the plane and chain bands affects the interpretation of the temperature dependence of the penetration depth and the infrared (ir) reflectivity. If each band is characterized by the ratio of the carrier density to the effective mass,  $n/m^*$ , then the relative size of this ratio is defined to be  $R_0 = (n_{pl}/m_{pl}^*)/(n_{ch}/m_{ch}^*)$ . We use the expressions for the effective mass of a two dimensional band (see previous paragraph) and of a one dimensional band ( $m_{ch} = 12(\hbar db/k_B)^2 n_{ch} \gamma_{ch}$ )<sup>26</sup> to show that  $R_0 = 4\pi db^2 n_{pl} \gamma_{ch} / \gamma_{pl}$  ( $d$  is the interplanar spacing  $(11.6\text{\AA})^5$ ,  $b$  is the distance between chains  $(3.88\text{\AA})^5$ ,  $n_{pl}$  is the density of carriers in the planes  $(2.86 \times 10^{21} \text{ cm}^{-3})^{28}$ ). Since the planes remain stable for oxygen deficiencies less than  $\delta = 0.2$ , we contend that  $R_0$  is affected mostly by the structural integrity of the chains. The specific heat data indicate that  $R_0$  is greater than or equal to 15, for fully oxygenated samples. This compares to the value of 3.5 determined from penetration depth measurements<sup>27</sup> in thin films and 0.5 from the ir reflectivity of untwinned single crystals.<sup>29</sup> Noting that the penetration depth data of Anlage et al.<sup>27</sup> are strongly dependent on the number of defects in the film, we expect that films with fewer chain defects would exhibit a higher value of  $R_0$ . Similarly, the value of  $R_0$  determined from ir reflectivity data should increase in samples with higher oxygen stoichiometry. In general, we speculate that the strong dependence of the measured electronic properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (i.e. specific heat

jump at  $T_c$ , penetration depth, and resistivity) on oxygen content is due to the large contribution of the chain band to  $D(\epsilon_F)$ .

The high temperature specific heat reveals much about the electronic and lattice dynamical properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Clearly, anharmonicity must be considered when calculating the lattice contribution to the specific heat from the phonon density of states determined from neutron diffraction data. The specific heat of the charge carriers is similar to the predictions for a Fermi liquid, but differs markedly from the temperature dependence expected of a gas of charged Bosons. Also, the experimentally determined electronic density of states is a factor of three larger than the value predicted by band structure calculations. The sensitivity of many measured electronic properties to the structural integrity of the chains can be attributed to the large fraction of the density of states at the Fermi level contributed by the chain band.

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### Figure Captions

- Figure 1. Relative enthalpy of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  between  $t$  and  $0^\circ\text{C}$ . The solid line through the data represents a polynomial fit to the data. See discussion preceding Eq. 1.
- Figure 2. The specific heat at constant volume vs. temperature for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , derived from the measured enthalpy data. See Eq. 1. The small circles are the low temperature data measured by Junod<sup>12</sup> et al. The lines represent the lattice specific heat determined by Eq. 2 (solid) and Eq. 3 (dotted).
- Figure 3. The electronic specific heat vs. temperature for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . In the inset, the lattice is assumed to be totally harmonic. For the main graph, the lattice contribution has been adjusted for anharmonic effects. The open and closed circles are defined as in Fig. 2.

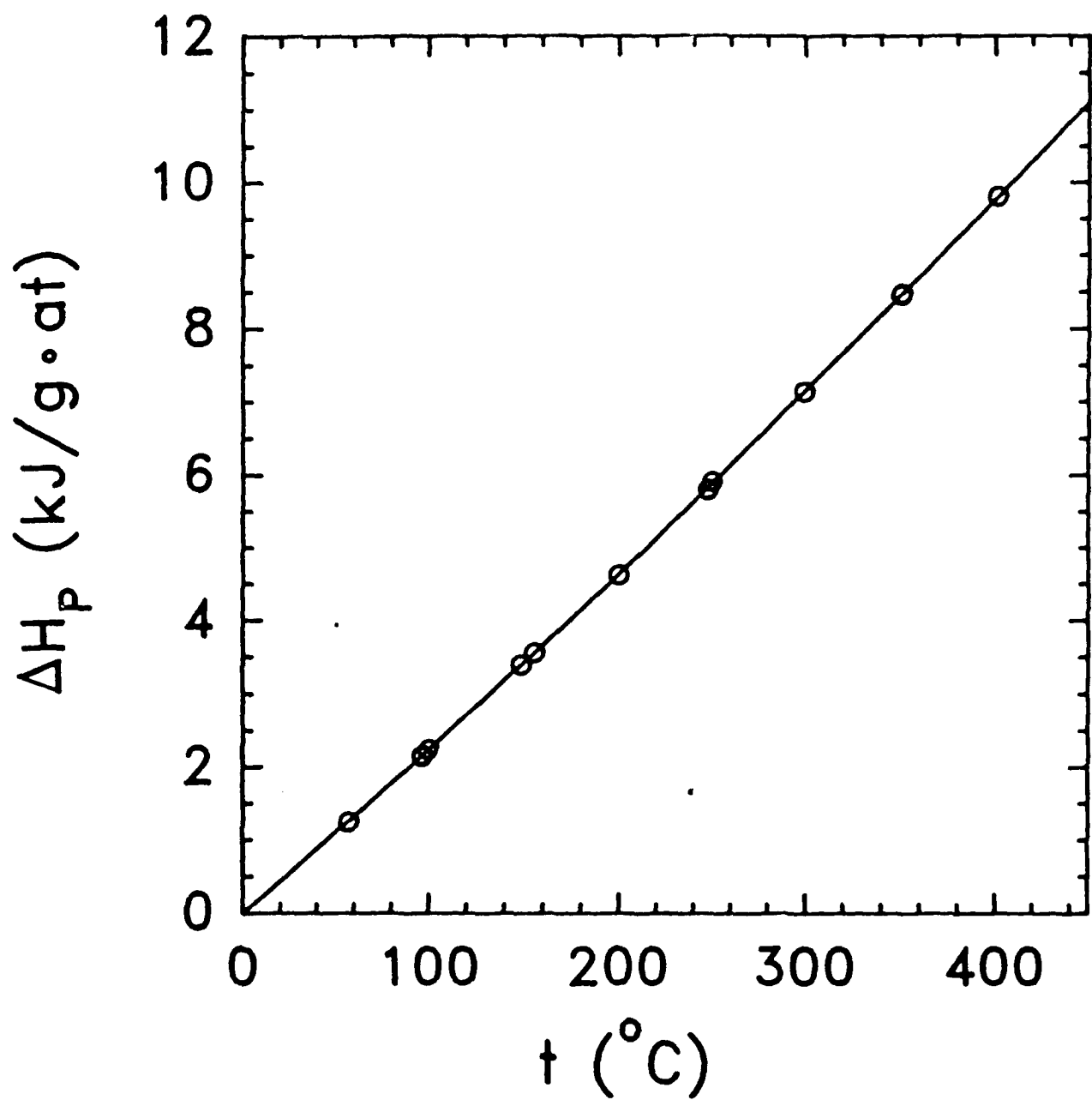


Figure 1

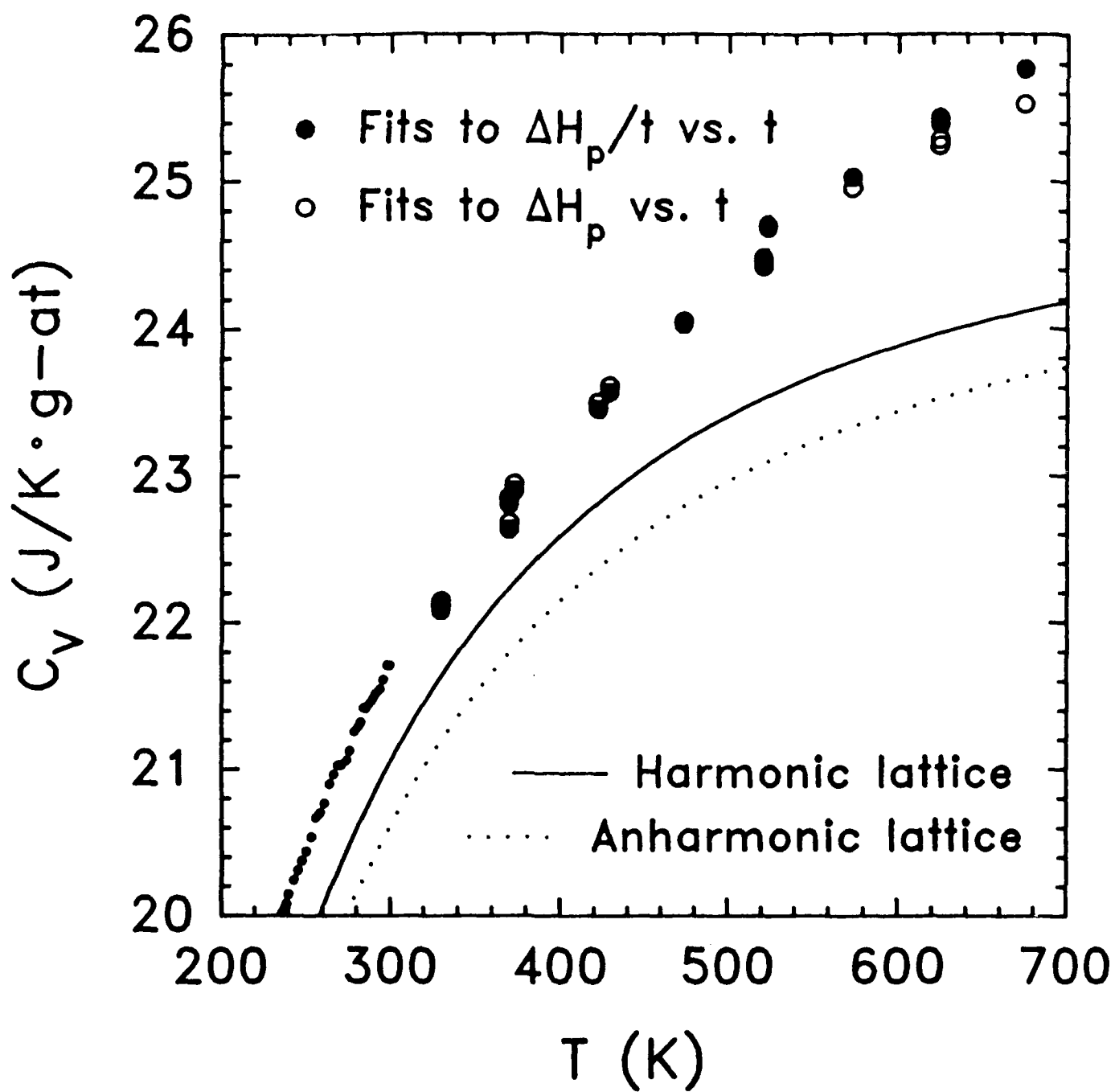


Figure 2

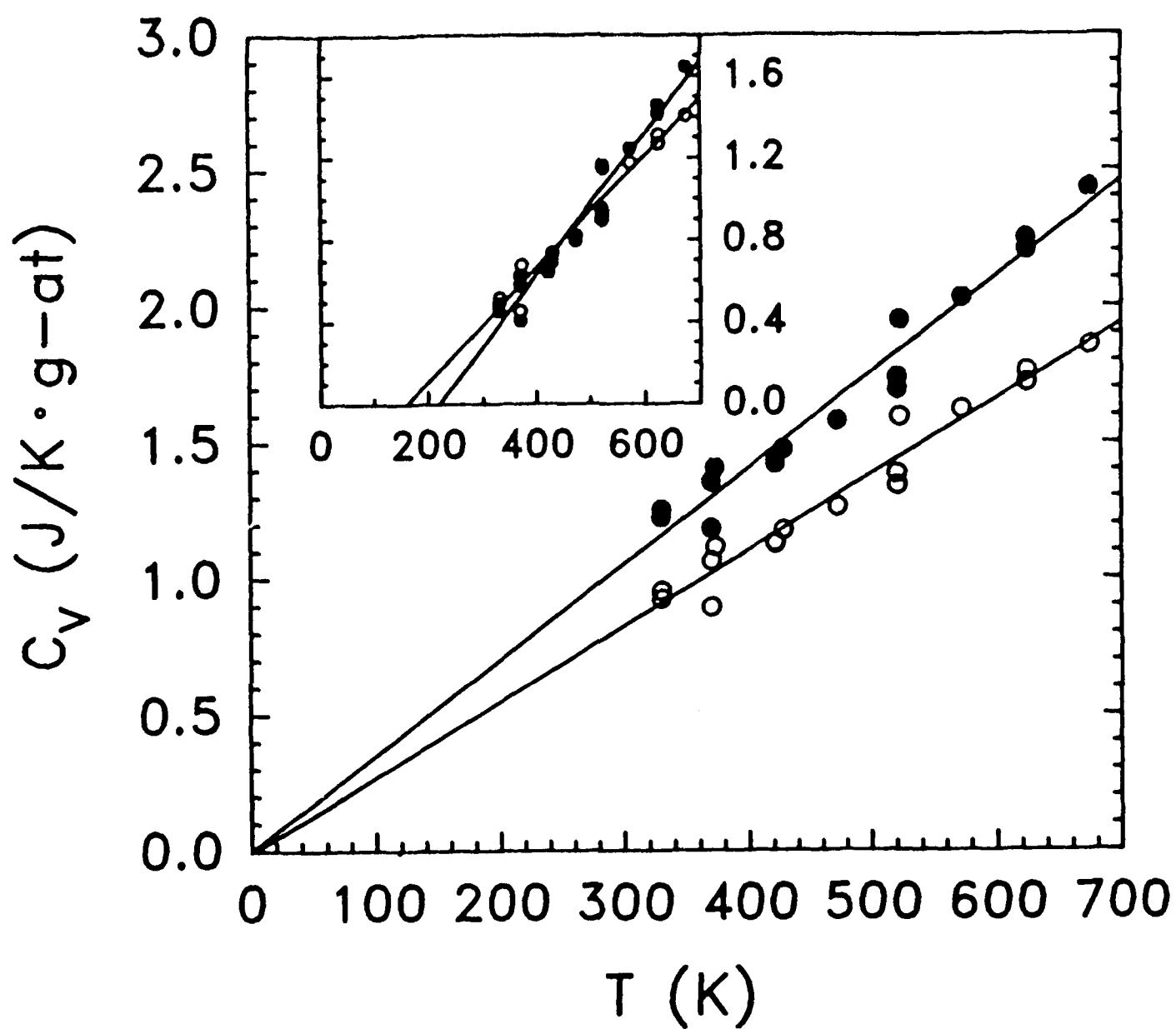


Figure 3